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A consideration of the nature of the subject taught will also furnish a guide for the employment of laboratory and didactic methods in the required and elective courses above suggested. In general the required courses, being comparatively elementary and concerned chiefly with the presentation of well ascertained facts, may be made demonstrative in their character and may be conducted in accordance with laboratory methods, though a short course of didactic lectures, parallel with laboratory work, will in most cases be found to be essential. In the elective courses which provide advanced instruction in many directions the limits of our knowledge will be more nearly reached. It will, therefore, be necessary to present and weigh the evidence for and against the various conflicting views which are almost certain to be held with regard to subjects lying within what Foster has called the 'penumbra' of solid scientific acquisition. For this purpose the most suitable method of instruction seems to be a short course of carefully prepared didactic lectures which should, however, be varied by demonstrations whenever the nature of the subject will allow.

It is, however, unnecessary to discuss these and other details at the present time. They will speedily arrange themselves as soon as the necessity for a comprehensive reform in our methods of medical instruction is generally recognized, and it is in the hope of helping to secure this recognition that I have addressed these remarks to you this evening. In whatever way the remedy is to come it should not be long delayed, for the difficulty of giving adequate instruction to constantly increasing classes seeking information over a constantly widening field of knowledge is felt each year with greater and greater keenness.

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ON THE INCREASING IMPORTANCE OF IN-ORGANIC CHEMISTRY.\*

WHENEVER a paper by Van't Hoff appears, it is read by chemists and especially by physical chemists, with unusual interest. This is due to the fact that the comparatively few papers which he has published have had such a marked influence on scientific thought, and on the development of those branches of knowledge to which he has devoted his energies.

The present lecture is probably the result of his observation, since he has been in Berlin, that by far the larger number of German chemists are devoting themselves to organic chemistry. At the same time that he recognizes the importance of this field of investigation, he utilizes this opportunity to call attention to the difference between the two branches of chemistry, organic and inorganic, and to point out some of the advances which have been made, especially in the latter. The main points of his lecture will be given partly in his own language, and partly as a free account of what was said.

The distinction between organic and inorganic compounds dates back some two hundred years. Those occurring in organic nature, in living things, were called organic, while those existing in the mineral kingdom were called inorganic. This division had, at the outset, a certain scientific justification, since inorganic chemistry had to deal with the comparatively simple problem of explaining the chemical transformations in dead matter, while organic chemistry dealt with the much more complex problem of the processes in living organisms.

While the original definitions of the two branches have changed somewhat as new facts have been discovered, yet this essential

\*Lecture before the 70th meeting of the Society of German Scientists and Physicians in Düsseldorf. — *Ztschr. f. Anorganische Chemie*, 18, 1.

difference still exists, that inorganic chemistry has to do with the relatively simpler, organic with the more complex problems. If we arrange the exact sciences in the order of increasing complication of the problems dealt with, we shall have inorganic chemistry more closely allied to physics, and organic chemistry to biology. The order would then be: Physics, inorganic chemistry, organic chemistry, biology.

Organic chemistry has now come to be the chemistry of the element carbon, while inorganic chemistry is that of the remaining 70 elements and their compounds. But we know that this distinction is not a sharp one, since sodium and calcium carbonates are treated in all works on inorganic chemistry. The two chief divisions of chemistry are, then, at present, best characterized by aim and method.

The more difficult problem in inorganic chemistry is the decomposition of substances into simpler compounds, and finally into the elements, so that the greatest triumph in inorganic chemistry is the discovery of new elements (Argon and Helium by Ramsay and Rayleigh). It finds the most complete expression of its results in the natural systems of Newlands, Mendeléeff and Lothar Meyer. The inorganic compounds are relatively simple, generally easy to obtain, and have a definite qualitative and quantitative composition.

The reverse is true in organic chemistry. Decomposition is easily effected, as by oxidation. The aim here is to synthesize compounds, and this is rendered difficult by the possibility of isomerism; substances being formed of the same composition, but of different constitution and properties. Organic chemistry triumphs in the artificial building-up of substances (the preparation of the different sugars by Fischer), and finds the most complete expression of its results in the structure theory and in stereochemistry.

The entirely different aims of the two branches of chemistry necessitate a corresponding difference of methods. As is well known, inorganic and organic chemistry are now studied independently. At the beginning of this century a great impulse was given to the study of chemistry by the discovery of the fundamental principle: "*The Mass of Matter does not change even in the most deep-seated transformations.*" At first the harvest was reaped chiefly in inorganic chemistry. The very important facts, discovered purely empirically—the impossibility of transforming one element into another, the weight and volume relations in chemical transformations—receive their hypothetical expression in the atomic and molecular conceptions and the molecular formula is the picture of the knowledge thus obtained.

Then came the harvest in organic chemistry. The methods of quantitative analysis were gradually adapted to the more complex relations in this field, and the constitution or configuration formula appeared, as a simple, clear picture of the relations. It indicated not only the kind and number of atoms in the molecule, but also their inner connections and their relative position.

Yet, organic chemistry has done comparatively little towards explaining the phenomena of life. The results of organic chemistry, expressed in the constitution formulas, are of relatively little significance for assimilation, etc. Also the knowledge of the constitution of albumin would thus be scarcely extended. "It appears to me as if this incapacity is conditioned also by the nature of the configuration formula. It represents the molecule as a solid unit, and corresponds, therefore, at best, to the relations which obtain at absolute zero, *i. e.*, at  $-273^{\circ}$ , and long before this all life processes are extinguished. The inner molecular state is explained for conditions under which life ceases."

Let us now look more closely at the condition of things at the present time. The discovery of thiophene by Victor Meyer, and Fischer's work on the sugars, are referred to. Notwithstanding the relatively small number of workers in inorganic chemistry in recent years, very brilliant results have been obtained. Those mentioned are: The discovery of the volatile compounds of iron and nickel with carbon monoxide, by Mond; of triazoic acid by Curtius; of six new elements by Ramsay; the artificial preparation of the diamond by Moissan; the carbides, selenides and borides, prepared by the same investigator.

Let stress be laid upon it that this experimental result is, in part, dependent upon the use of electricity, which is applicable chiefly to inorganic compounds. Let us examine more closely the details of this application; what electricity has already done, on the one hand as a source of higher temperatures, on the other as a means of effecting separations.

Electricity as a source of heat is of fundamental importance. The temperatures which can be reached by combustion processes are limited. By this means we cannot obtain temperatures very much above  $3,000^{\circ}$ . In the electric furnace temperatures as high as about  $4,000^{\circ}$  can be reached.

The electric furnace, in the hands of Moissan, has opened up a new way of preparing valuable and important substances. It is evident that this applies chiefly to inorganic chemistry. Higher temperatures do not form, but break down the molecular complexes which constitute the problems of organic chemistry. Our own existence, which depends chiefly on the interaction of such complex molecules, cannot be continued up to  $50^{\circ}$ . The compounds of the hydrocarbons which were obtained in the electric furnace, as carborundum and calcium carbide, have no

value for the synthetical processes of organic chemistry.

If we turn to electricity as a means of separation, it is self-evident that it can be only indirectly applied to organic chemistry, whose chief aim is synthesis. Most of the organic compounds do not belong to the electrolytes, which can be broken down by electrolysis. Most of the metals can, however, be separated by the current, in a form suitable for weighing, by using the proper intensity of current, and can be separated from one another by using a suitable electromotive force. The halogens have recently been separated in the same manner. A step is thus taken for inorganic analysis, which is comparable to the work of Liebig on the analysis of organic substances.

What has been accomplished by the use of electricity in separating the metals on a large scale, can be seen from the following data: In 1897 one-third of the entire copper produced (137,000,000 kilograms) was obtained electrolytically. The larger part of the gold and silver were obtained in the same way. Sodium is produced entirely by electrolysis (260,000 kilograms in 1897), and the increase in the aluminium produced, from 9,500 kilograms in 1888 to 321,000 kilograms in 1894, is to be referred to the same cause. This aluminium can now be used for the preparation of other metals which were difficult to obtain. At the last meeting of the Electrochemical Society in Leipsic we saw almost chemically pure chromium prepared by suitably igniting a mixture of aluminium and chromium oxide. In the same manner, manganese, titanium, tungsten, vanadium, cerium, etc., were formed. This opens up a field in the metal alloys, which will, perhaps, be of technical importance.

We thus see inorganic chemistry teeming with remarkable discoveries, enriched by a new method of preparing substances, and

simplified analytically. The ground is also unusually fruitful for applying and developing the fundamental generalizations which have been reached in chemistry in the last few years.

When, in 1843, Kopp declared that a new stage of development in chemistry would follow the period of quantitative investigation, first by union with another branch of science, he saw in advance what is now being effected in the union of chemistry and physics, which is being accomplished by the new physical chemistry. Let us call attention to the importance of applying the two fundamental principles of thermodynamics to chemistry, and how far consequences derived from these principles can be subjected to experiment, and what the result is.

The problems solved in this way, belong to the most important of our science, but receive a solution which has so little in common with our atomic and structural conceptions that they often do not appeal to chemists trained in the latter school. By this means problems will be solved, also biological problems, which lie out of the scope of the configuration method. By applying thermodynamics to chemistry it is chiefly inorganic chemistry which is advanced.

We must mention first the problem of affinity. Thermodynamics does not refer affinity to the reciprocal action of atoms, but measures affinity by the maximum work which the reaction can perform. Let us consider reactions which take place with increase in volume, say the union of copper and calcium acetates to form the double salt. If this reaction takes place in a closed vessel, the walls are broken. On the other hand, the reaction can be hindered by bringing a counter pressure to bear on the salts, say by a piston and cylinder; and Spring has actually shown that the double salt can be broken down by subjecting it to several thousand atmospheres of pressure. This counter pressure, which just prevents the re-

action, is very closely connected with affinity regarded as force, and affinity is determined as work by the mechanical work which is done by the reaction against the maximum pressure.

The reaction may complete its maximum work in other ways, as in an electric battery, and it can then be measured from the electromotive force of the battery.

We arrive, in this way, at a generalization of very great importance:

*A transformation will, then, only take place of itself in case it is in a position to do a positive amount of work. If the amount of work done is negative the transformation can only take place of itself in the opposite sense. If the work done is zero it can take place in neither sense.*

This work and the possibility of reaction depending upon it, can be calculated in any given case, provided the work is ascertained, once for all, which is done when each of the substances in question is formed from the elements. This work can be expressed, *e. g.*, in calories. This 'work of formation,' by simple addition and subtraction, leads to the 'work of transformation,' the sign of which conditions the possibility of the transformation. This program has been carried out, to a certain extent for the mercury compounds, by Nernst and Bugasky. It should be mentioned that from this principle it was foreseen that mercurous chloride must be decomposed by potassium hydroxide, although the transformation takes place with heat absorption.

We have obtained, also, a generalization for reactions which only partly complete themselves, on account of the introduction of the opposite reaction, which leads to a condition of so-called chemical equilibrium, as in the combination of iodine and hydrogen, and in etherification. It is essential that, in such cases, changes in concentration should be produced during the reaction, and on account of the reaction. These decrease the work of transformation, finally

bringing it to zero, whence the reaction velocity gradually decreases and finally, also, becomes zero. In the union of iodine and hydrogen the increasing concentration of the hydriodic acid formed, introduces a gradually increasing opposing force, which finally brings the reaction to rest.

There is thus obtained a further principle, applicable in many directions. The point at which a reaction comes to rest can be calculated from the work of transformation. This was strikingly confirmed very recently by Bredig and Knüpfner, on the basis of measurements of electromotive force; it was accurately determined when the double decomposition of thallic chloride and potassium sulphocyanate came to rest.

But also the change in work of transformation through changes in temperature, pressure and mass can be calculated from thermodynamics, and also the consequent shifting of the point of equilibrium. Quantitatively expressed, this shifting always takes place in the sense that cooling favors whatever is formed with evolution of heat, until finally, at absolute zero, all reactions are completely displaced in this sense. Then the course of the reaction would be conditioned by the 'heat of transformation,' which, at zero, would be equal to the work of transformation.

In studying equilibria from this standpoint, not only the *existence* of every substance, but also the *conditions of existence*, are determined. And it may be added, not only the conditions of existence of individual substances are determined, but also all the compounds which it is possible to obtain from given materials, say water and salt. The reinvestigation of magnesium chloride from this standpoint gave not less than six different hydrates.

This method of investigation closely resembles the complete survey of a region where formerly only individual cities and villages were recorded. In the not very

distant future inorganic chemistry may do for geology what it has already done for mineralogy in the preparation of individual minerals.

The views here expressed will be of chief service in inorganic fields, since two obstacles are in the way of applying them to organic chemistry: First, the great possibility of compound formation. A single pair of substances, as carbon and hydrogen, gives rise to an unlimited series of compounds. Second, the very sluggish manner in which organic transformations take place, causes reactions which are possible, to proceed very slowly, or not to take place at all. Thermodynamics stands here, in its application, as before a very complex engine which is rusted until it is useless.

But the application of thermodynamics to chemistry has been made in another direction, and here the physical chemistry of to-day has found its most fruitful field. The possibility of determining the molecular weight of dissolved substances is given by the so-called osmotic methods. A very great need of inorganic chemistry would thus be met. The molecular weights of organic compounds, which are often volatile, were generally known by determinations of vapor-density. The inorganic compounds investigated in this respect were, on the other hand, exceptions. The work of a few years has sufficed to fill up these omissions.

We arrive, then, at our last point, a consequence of these osmotic methods, that electrolytes—salts, acids and bases—are broken down in aqueous solution in a peculiar manner. The only explanation which meets the case is that of Arrhenius, according to which a dilute solution of, say hydrochloric acid, would contain instead of molecules of acid, negatively and positively charged atoms of chlorine and hydrogen.

It is still impossible to pass final judg-

ment on this fundamental change of our conceptions, yet it is a fact that the most widely different properties of solutions agree qualitatively with the new conceptions. Quantitatively, the result calculated agrees very nearly with that found, but, thus far, the agreement is not always perfectly satisfactory. It is of chief importance for our purpose that a new impulse was thus given to the study of solutions of salts, acids and bases, *i. e.*, chiefly to inorganic compounds.

A final remark in closing: While it has been repeatedly emphasized, in the foregoing that it is chiefly inorganic chemistry that has been advanced by the new theoretical considerations, yet it is not meant that organic chemistry has thus lost in interest. On the contrary, the science of chemical equilibrium can be applied also here, and has already been thus applied.

The action of ferments is then taken up, and the work of Tammann and others cited to show that such act, at least in some cases, to only a limited extent, a condition of equilibrium being reached before the decomposition is complete. Thus, amygdalin is only partly broken down by emulsin, and the breaking-down goes farther if the decomposition products are removed. If, on the contrary, he had added the decomposition-products he would, perhaps, have effected the synthesis of amygdalin. In case the ferment is not changed by its action, on theoretical grounds a condition of equilibrium must be introduced, and not a total transformation, and, therefore, the opposite reaction should be realized. It is a fair question to ask whether (from the science of equilibrium) sugar cannot be formed from carbon dioxide and alcohol, under the influence of zymase, when the pressure of the carbon dioxide exceeds a certain limit; and also whether trypsin is not in the position, under conditions given by the science of equilibrium, to form albu-

min from the decomposition products which it itself yields?

"If I have gone too far in these last expressions they may remain as proof that I always have a warm heart for organic chemistry." Van't Hoff concluded with the wish that Germany, which is in danger of being surpassed in inorganic chemistry by other nations; which has recently lost from this field such men as Victor Meyer, Lothar Meyer, Gerhard Krüss and Clemens Zimmermann, will soon again occupy a leading position, through the choice of young men of our science to enter this field.

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JOHNS HOPKINS UNIVERSITY,  
November, 1898.

#### *THE TAILLESS BATRACHIANS OF EUROPE.\**

THE anurous salient amphibians, or tailless batrachians, have been long favorite subjects of study in Europe, and much has been written upon their habits. Only a few years ago (in 1890) Dr. J. de Bedriaga published an elaborate monograph of the Amphibians of Europe (*Die Lurchfauna Europas*) giving very full descriptions of the species and their manner and customs. Now we have completed a still more elaborate work on a single order of Amphibians—the Salientia—including the frogs and toads and their relations. This work, entitled 'The Tailless Batrachians of Europe,' is by Mr. G. A. Boulenger, and has been 'issued to the subscribers to the Ray Society,' in two bound volumes or parts for the years 1896 and 1897; the pagination is continuous from the first into the second volume (pp. 211–376). Doubtless many of the 'subscribers' will rejoice in the diversification of the subjects monographed, for nearly a

\* *The Tailless Batrachians of Europe.* By G. A. Boulenger, F.R.S. London: printed for the Ray Society. 1897–1898. 2 parts, 8vo., t. p., iii, 376 pp., 24 pl., 7 maps.